Kinetics of 4,4'-Diaminodiphenylmethane Curing of Bisphenol-S Epoxy Resin

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ABSTRACT: The kinetics of the cure reaction for a system of bisphenol-S epoxy resin (BPSER), with 4,4'-diaminodiphenylmethane (DDM) as a curing agent, were studied by means of differential scanning calorimetry (DSC). Analysis of DSC data indicated that an autocatalytic behavior showed in the first stages of the cure, with the model proposed by Kamal, which includes two rate constants, k_1 and k_2 , and two reaction orders, m and n. Rate constants k_1 and k_2 were observed to be greater when curing temperature increased. The over-all reaction order, m + n, is in the range of 2.5 \sim 3. The activation energies for k_1 and k_2 were 55 kJ/mol and 57 kJ/mol, respectively. Diffusion control is incorporated to describe the cure in the latter stages. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1799–1803, 1999

Key words: bisphenol-S epoxy resin; 4,4'-diaminodiphenylmethane; cure reaction; kinetics; differential scanning calorimetry

INTRODUCTION

Epoxy resins based on epichlorohydrin (ECH) and bisphenol-S (BPS) have better heat resistance, gel time, and mechanical properties than those of epoxy resins prepared from ECH and bisphenol-A (BPA).^{1,2} The bisphenol-S epoxy resin (BPSER) has been synthesized, and the kinetics of this epoxy resin formation have been studied.^{3–5} However, the data and description of cure reaction kinetics and other fundamental theory about application of BPS epoxy resin with amines have been lacking until now.

Curing kinetics of epoxy resins have been studied with different techniques, such as infrared spectroscopy (IR) and thermal analysis as differential scanning calorimetry.^{6,7} Because of the complex chemistry involved in epoxy curing, a phenomenological approach is the most popular for these systems. The models arising from proposed kinetic mechanisms

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Journal of Applied Polymer Science, Vol. 73, 1799–1803 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/091799-05 have been used as autocatalytic cure kinetics.^{6,8} In general, a good fit to experimental data was obtained in the early stages of the cure, but deviations were observed in the later stages, particularly near vitrification, when the reaction is primarily diffusion controlled.

In the work to be described herein, the DSC technique was used to study the curing kinetics of bisphenol-S epoxy resin with 4,4'-diaminodiphenylmethane (DDM). The results of our initial phenomenological approach to describe the curing kinetics of neat resin have been reported in the literature.^{9,10} The curing reactions in the kinetic control stage follows autocatalytic kinetics and a four-parameter, semiempirical equation proposed by Kamal.⁸ To our best knowledge, this is the first time that such a model and diffusion controlled process has been applied to the BPSER–DDM system.

EXPERIMENTAL

Materials

Bisphenol-S was recrystallized from the toluene, and a crystal with a melting point of 240°C was obtained. Epichlorohydrin, NaOH, KOH, acetone, ethylalcohol, and hydrochloric acid were all analytically pure grade and were supplied by Beijing Chemical Reagent Co.

Synthesis of BPSER

Epoxy resin based on bisphenol-S used in this work was synthesized according to Rainer et al.¹¹



where $n = 0 \sim 1$. The epoxy value was determined according to Jay¹² to be 0.31 mol/100 g.

Method

DSC measurements were carried out using a Shimadzu DT-40 thermal analyzer. The DSC was calibrated with high-purity indium, α -Al₂O₃ was used as the reference material. Isothermal and dynamic heating experiments were carried out according to Opalicki et al.⁶ under a nitrogen flow of 40 mL/min.

The reactants BPSER and DDM were mixed under 5°C in a 1 : 1 equivalent ratio. Approximately 10 mg samples of the mixture were weighed accurately into an aluminum DSC sample pan and covered with an aluminum lid. The entire operation was carried out in a dry chamber.

Isothermal DSC analysis was performed at temperatures ranging from 80 to 105°C in 5°C increments. The furnace was first heated to a desired fixed temperature and kept for a certain period of time. When the system reached the equilibrium state, the sample was quickly set on the calorimetric detector plate. The reaction was considered complete when the rate curve leveled off to baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of reaction, was used to calculate the isothermal heat of cure, ΔH_1 , at a given temperature. After each isothermal run, the sample was cooled rapidly in the DSC cell to 10°C and then reheated at 10°C/min to 250°C to determine the residual heat of reaction, ΔH_r . The total heat evolved during the curing reaction was $\Delta H_0 = \Delta H_i + \Delta H_r$.

The dynamic DSC analysis was performed at four different heating rates: 5, 8, 10, and 15°C/ min from 10 to 250°C. The total heat of reaction ΔH_0 was estimated by drawing a straight line connecting the baseline before and after the peak and integrating the area under the peak.

RESULTS AND DISCUSSION

The mechanism of the curing reaction of thermosetting resins have the two general kinetic models; that is, *n*th-order and autocatalytic mechanism.⁷ The *n*th-order kinetics can be expressed as

$$d\alpha/dt = k(T)(1-\alpha)^n \tag{1}$$

The autocatalytic kinetics can be expressed by Kamal⁹ as

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m) (1 - \alpha)^n \tag{2}$$



Figure 1 Conversion, α , versus time curves at different temperatures.

The molecular structure of this resin has the following approximate form.



Figure 2 Reaction rate, $d\alpha/dt$, versus time curves at different temperatures.

where α is the extent of reaction, and α is given by $\alpha = \Delta H_t / \Delta H_0$. ΔH_t is the partial area under a DSC trace up to time t; k, k_1 , and k_2 are the specific rate constants at these models, which are the functions of temperature; and m and n are the reaction orders. According to nth-order kinetic model, the maximum reaction rate will be observed at t = 0, and according to the autocatalytic model, the reaction rate is zero initially and attains a maximum value at some intermediate conversion.

Isothermal DSC

If the cure reaction is the only thermal event, then the reaction rate $d\alpha/dt$ is proportion to the heat flow, dH/dt; that is,

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \tag{3}$$

The rate of cure can be determined by the curing exotherm.

Figure 1 shows plots of conversion α versus time *t* at different isothermal temperatures, and isothermal DSC curves are shown in Figure 2

plotted as $d\alpha/dt$ versus time. The reaction rate at any temperature is seen to increase with time at the initial stage of cure and passes through a maximum, while the reaction rate peak becomes higher and shifts to lesser times with an increase in isothermal temperature.

The plots show a maximum reaction rate at time t > 0, thereby negating simple *n*th-order kinetics. The autocatalytic kinetic model is appropriate to describe this isothermal curing behavior. In eq. (2), m + n is the over-all reaction order. The kinetics parameters can be obtained by fitting the isothermal data with nonlinear least-squares procedures, and they are shown in Table I.

It is observed that the k_1 values were small compared with that obtained for k_2 , which affects the reaction more. Furthermore, k_1 and k_2 values are observed to increase with increasing temperature, respectively. The over-all reaction order, m+ n, is largely in the range 2.5 \sim 3.

The reaction rate constants k_1 and k_2 depend on the temperature following the Arrhenius relationship.

$$k = A \exp(-E/RT) \tag{4}$$

Rate constants k_1 and k_2 are shown as an Arrhenius plot in Figure 3, $-lnk \sim 1/T$, which yields the values of 55 KJ/mol and 57 KJ/mol for the associated activation energies E_1 and E_2 . It is observed that the linear correlation coefficients for k_1 values is 0.9904 and for k_2 is 0.9596.

The values of *m* and *n* obtained for each curing temperature are shown in Figure 4, and *m* varies from 0.5 to 1, and *n* is 2 to 2.3 (*n* is larger than 2.3 when temperature is high at T = 105 °C).

Comparison between typical experimental DSC data under two temperatures 95°C and 105°C and predictions of the autocatalytic model, with values of model parameters determined above, are shown in Figure 5. Good agreements are obtained for the initial stage of reaction;

Table I Kinetic Parameters for Isothermal Curing of BPSER/DDM

<i>T</i> (°C)	80	85	90	95	100	105
$k_1(\times 10^{-4})$	4.266	5.498	7.171	9.869	10.396	15.412
$k_{2}(\times 10^{-3})$	1.247	1.390	1.794	3.385	3.594	3.936
m	0.52	0.52	0.65	0.81	0.73	0.94
n	1.94	2.01	1.79	2.23	2.28	2.71
m + n	2.46	2.53	2.44	3.04	3.01	3.65



Figure 3 Rate constants of curing reaction, k_1 and k_2 , versus temperature.

whereas, deviations are observed when the conversions beyond 40% at 95°C and 50% at 105°C. This is attributable to the onset of gelation and becomes the diffusion control. Differences between model predictions and experimental data are observed to be greater when curing temperature decreases under the same conversion.

Diffusion-Controlled Reaction

To consider the diffusion effect, we introduced a diffusion factor $f(\alpha)$, according to Opalicki et al.⁶ and defined as the ratio k_e/k_c , k_c , being the rate constant for chemical kinetics and k_e the over-all effective rate constant. This diffusion factor is given by



Figure 4 Estimated values of m and n at different curing temperatures.



Figure 5 Comparisons of experimental data with model prediction: reaction rate, $d\alpha/dt$, versus conversion α at 95°C and 105°C.

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]}$$
(5)

where α_c is the critical conversion, and *C* is the diffusion coefficient. When α is much smaller than the critical value $\alpha \ll \alpha_c$, the $k_e = k_c$, then $f(\alpha)$ approximates unity, the reaction is kinetically controlled, and the effect of diffusion is negligible. As α approaches α_c , $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$ and beyond this point, approaches zero as the reaction effectively stops. It shows that with conversion increasing, the effect of diffusion developed gradually. The effective reaction rate k_e at any conversion is equal to the chemical reaction rate k_c multiplied by $f(\alpha)$.

Figure 6 shows the plots of $f(\alpha)$ versus conversion α at different curing temperatures. As the cure progresses, and the resin crosslinks, the glass transition temperature T_g of the system rises. When it approaches the curing temperature, the resin passes from a rubbery state to a glassy state. At this stage, the mobility of the reacting groups is hindered, and the rate of conversion is controlled by diffusion rather than by chemical factors. The k_e

and $f(\alpha)$ are decreased with the conversion increasing, and approach zero when the glass transition temperature T_g is raised.

Dynamic DSC

When the dynamic method was used to investigate the curing process of the BPSER/DDM system, the measurements were taken at various heating rates: 5, 8, 10, and 15°C/min, in a nitrogen atmosphere. The results show that the extent of reaction at the exothermal peak α_p was a constant (Fig. 2). So, the apparent activation energy E_a of this curing process can be calculated by the Ozawa method⁸:

$$E \simeq \frac{-R\Delta \log \phi}{0.4567\Delta (1/T_p)} \tag{6}$$

where R is the gas constant, ϕ is the heating rate, and T_p is the temperature at the exothermal peak value. Rearranging eq. (6) yields

$$\ln \phi = C - 1.052 \frac{E}{RT_n} \tag{7}$$

where C is the constant.

Figure 7 shows the plots of heating rate ϕ versus peak temperature T_p . The apparent activation energy E_a is obtained from linear regression analysis as 49.80 KJ/mol, and the value is approximate to the value obtained from isothermal DSC results.

CONCLUSIONS

1. The cure reaction for the system of BPSER/ DDM is shown as an autocatalytic behavior



Figure 6 Plot of diffusion factor, $f(\alpha)$, versus conversion at different curing temperatures.



Figure 7 Heating rate, ϕ , versus peak temperature T_p .

and can be described with the model proposed by Kamal, which includes two rate constants k_1 and k_2 and two reaction orders m and n. The over-all order m + n is in the range 2.5 \sim 3.

2. In the first stages of the cure, the reaction is chemically kinetically controlled. The active hydrogen atom of the curing agent amine combines with epoxies, so the crosslinking structure appears. In the latter stages (up to 40% conversion), the reaction is controlled by diffusion.

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